AD-A081 644 COAST GUARD WASHINGTON DC F/6 8/7
U.S. COAST GUARD LIQUEFIED NATURAL GAS RESEARCH AT CHINA LAKE.(U)
JAN 80 A L SCHNEIDER, C D LIND
UNCLASSIFIED USCG-M-03-80 NL

END
DATE FILMED
4 80
DTIC

Technical Re

(14) 1. Report No. USCG-M-03-80

2. Government Accession No.

3. Recipient's C (11)

4. Title and Subtitle (6) U.S. Coast Guard Liquefied Natural Gas Research at China Lake

5. Report Date 1 Jan

6. Performing Or

(10)

7. Author(s) Dr. Alan L. Schneider, C. Douglas Lind, Dr. Michael C. Parnarouskis

8. Performing Or

9. Performing Organization Name and Address

10. Work Unit No.

11. Contract or G

12. Sponsoring Agency Name and Address
Commandant (G-MHM/14)
U.S. Coast Guard Headquarters
Washington, D.C. 20593

(9) Final

13. Type of Report

14. Sponsoring Ag

15. Supplementary Notes

16. Abstract

For the past decade the Coast Guard has been studying the b Liquefied Natural Gas (LNG) and similar flammable, liquefied gas of its efforts in marine safety. In recent years this effort ha concentrated at the U.S. Naval Weapons Center, China Lake, Calif program included such liquefied gases as propane, butadiene, and A comprehensive test program was developed, including the prepar theoretical model for deflagration to detonation transition; sho to develop the properties of confined deflagration and detonatio and cloud fires, of both LNG and Liquefied Petroleum Gas (LPG); development of gas sensors and their testing in the field. From has come a better understanding of the consequences of liquefied gas spills in general and LNG spills in particular; specifically combustion of methane is generally of a lower order than that of liquefied gases, and that unconfined LNG vapor clouds are unlike Importantly, models for LNG pool and cloud fires have been devel several new gas sensors have been developed and have undergone f

17. Key Words
Liquefied Natural Gas
Methane, LNG, Pool Fire, Cloud Fire

Hazardous Materials, Cryogenic Liquid

18. Distribution Statement
Document is available through the National Information Service,

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of

Form DOT F 1700.7 (8-72)

Reproduction of completed page authorized

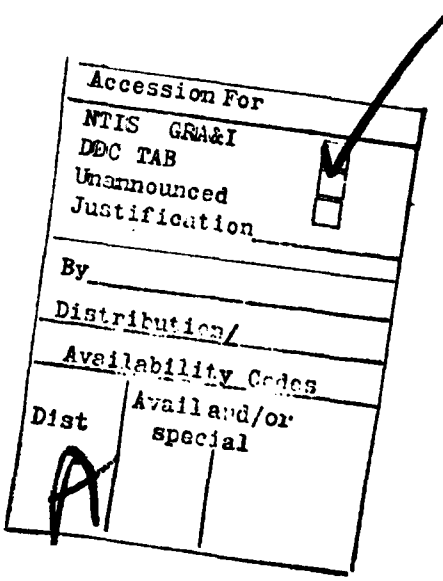
1086450

U.S. Coast Guard Liquefied Natural Gas Research at China Lake

Alan L. Schneider, Sc. D. Chemical Engineering
Office of Merchant Marine Safety
U.S. Coast Guard Headquarters
Washington, D.C.

C. Douglas Lind, Ph.D. Chemistry
Explosives Technology Branch
Ordinance Systems Department
U.S. Naval Weapons Center
China Lake, California

Michael C. Parnarouskis, Ph. D. Chemistry
Office of Research and Development
U.S. Coast Guard Headquarters
Washington, D.C.



ACKNOWLEDGEMENT

The authors gratefully acknowledge the assistance of the Arthur D. Little Co., Inc. for analyzing and interpreting the results from the Liquefied Natural Gas pool fire and cloud fire tests and in preparing mathematical models of these tests.

ABSTRACT

For the past decade the Coast Guard has been studying the behavior of Liquefied Natural Gas (LNG) and similar flammable, liquefied gases as part of its efforts in marine safety. In recent years this effort has been concentrated at the U.S. Naval Weapons Center, China Lake, California. This program included such liquefied gases as propane, butadiene, and ethylene oxide. A comprehensive test program was developed, including the preparation of a theoretical model for deflagration to detonation transition; shock tube test to develop the properties of confined deflagration and detonation; large pool and cloud fires, of both LNG and Liquefied Petroleum Gas (LPG); and the development of gas sensors and their testing in the field. From this work has come a better understanding of the consequences of liquefied flammable gas spills in general and LNG spills in particular; specifically that the combustion of methane is generally of a lower order than that of most other liquefied gases, and that unconfined LNG vapor clouds are unlikely to detonate. Importantly, models for LNG pool and cloud fires have been developed. Finally, several new gas sensors have been developed and have undergone field testing.

This study has given government and industry a better understanding of LNG and other liquefied gases. The authors are confident that safe transportation is feasible.

The views and opinions expressed in this paper are those of the authors, who are solely responsible for the accuracy of facts and data presented. This does not necessarily represent policy or official views of the U.S. Coast Guard or of the U.S. Navy.

INTRODUCTION

Hazardous materials have increasingly become the subject of public and governmental concern. Liquefied gases, especially Liquefied Natural Gas (LNG) and Liquefied Petroleum Gas (LPG), have increased in use in recent years - and paralleling this growth in use has been an increase in concern about their safety. Hazardous cargoes present a greater danger to the public as, year after year, the number of hazardous materials aboard ship increases and the amount of hazardous materials aboard each ship increases as well. In the United States, the Coast Guard is charged with the protection of life and property from harm due to marine transportation. By developing a body of regulations affecting each facet of marine shipping, the Coast Guard intends to reduce the hazard to the public and to the marine industry to a low, acceptable level. While a complete knowledge of all aspects of each hazardous cargo is desirable, often this information is not available and so the Coast Guard must embark on a research program to develop this information. With the vast and increasing number of commodities in marine commerce and with the limited research funds available, the Coast Guard has had to design its research program very carefully. A consistent practice is to evaluate a single chemical or a small number of chemicals to represent a large group. One such group is the liquefied gases. This paper discusses the research conducted at the Naval Weapons Center (NWC), China Lake, California, under the direction of the U.S. Coast Guard.

This program had its beginning in the late 1960s, when the Coast Guard recognized that the large scale shipment of liquefied gases was imminent, especially the shipment of vast quantities of LNG. A large scale study of the properties and hazards of LNG would not only help to insure the safe transportation of LNG but would help in understanding the behavior of such liquefied gases as LPG, propylene oxide, and butadiene. Therefore in 1968 the Coast Guard contracted with the U.S. Bureau of Mines for a study of LNG. In this and a succeeding study, the emphasis was on the effects of LNG spills onto water, including the cryogen's spreading rate on water, its vaporization rate, and its vapor dispersion. There were two important and surprising findings: when spilled onto water, no coherent ice layer formed, and the vaporized LNG was so cold that the resulting vapor-air cloud density was greater than that of air at ambient temperature. Without ice formation, the vaporization flux was constant with time, and did not decrease with time as might be expected if ice formed; with the vapor-air mixture density being greater than ambient air, the vapor cloud remained close to the water and persisted longer than if it were naturally buoyant. These two results together meant that a spill of LNG could generate a vapor cloud that could travel downwind long distances before becoming sufficiently diluted that the cloud was no longer flammable. Therefore even if a spill occurred some distance from a port, the cloud, or so it seemed at the time, might endanger that port (Burgess et al, 1970 and Burgess et al, 1972). These findings, together with the report of an

occasional but violent interaction between the cryogen and water, stimulated widespread interest in the spill on water and the vapor cloud dispersion problems.

The Coast Guard's interest then turned to the combustion of LNG and similar liquefied gases. Deflagration (fire) and detonation (violent explosion) are, in general, the major hazards of hydrocarbons, and with as much as 55,000 tonne of LNG in just one ship, combustion of the cargo is the major danger in an accident. Although the Bureau of Mines work included a single fire test, it was small and intended only to be qualitative. For the new study the Coast Guard contracted with the Naval Weapons Center (NWC) to conduct a series of large scale field tests. Without the financial aid of the Energy Research and Development Administration, the Department of Energy, the Office of Pipeline Safety Operations, the National Aeronautics and Space Administration, the American Gas Association, and the Gas Research Institute, this work could not have been completed. The goal of this project was to develop a mathematical model for pool fires and vapor cloud fires, and to investigate the likelihood of unconfined vapor cloud detonations. Several other topics related to these issues were also studied. The results of the work have proven very useful to the Coast Guard's regulatory effort -but more importantly, have demonstrated that, with proper precautions, LNG can be transported safely.

THEORETICAL MODEL

At the beginning of this project, Professor Forman A. Williams of the University of California, San Diego, prepared a theoretical model for unconfined vapor cloud explosions entitled "Qualitative Theory of Non-Ideal Explosions." His objective was to develop a mathematical model of such explosions and, in particular, to develop a method for estimating such important initial conditions as the critical spill sizes necessary for a Deflagration to Detonation Transition (DDT). Direct initiation of a vapor cloud detonation such as by solid high explosive was not considered. Due to the complexity of these combustion phenomena, only a qualitative approach was considered appropriate. Spherical, hemispherical, and cylindrical geometries were considered in modeling deflagrative behavior, including flame speed and overpressures. In evaluating the DDT event, two mechanisms were investigated, flame accelerations due to turbulence, and thermal explosion in the fuel-air mixture in front of the flame front, caused by the shock front heating the unburned mixture. The principle was that the strength of the shock wave generated by the deflagration could be increased by these mechanisms to a detonation. Williams concluded that for methane the thermal explosion mechanism was unlikely to result in detonation unless the deflagration shock wave was fairly high; as the pressure decreased, the ignition time increased dramatically. With a pressure ratio across the shock front of 3, the ignition would be 10^{10} sec; such delay times would require unrealistically

large clouds for a DDT. Furthermore, the pressure ratios in the weak ignition hemisphere tests described below were found to be far below 3. For this reason, Williams concluded that turbulence would be the likely mechanism for the DDT. This conclusion supported the placement of obstacles in the path of the flame front so as to increase the flame turbulence. Such obstacles were used in the weak ignition series of hemisphere tests. Lind has presented Williams' formulation in Lind, 1974.

SHOCK TUBE TESTS

In order to provide data on deflagation and detonation properties, a shock tube facility was built to produce both confined deflagration and detonations. The tube was built of steel, and was 0.6 m in diameter and 3.6 m long for deflagrations but, for detonations, it was only 1.8 m long. Provision was made for introducing the test gas and the ignitor; thermocouples for measuring the flame velocities and piezoelectric gauges for measuring pressures were built into the tube. Deflagration was initiated using a 3 kV, 10.5 J spark and detonation was initiated with 90 g of sheet explosives (5 g was used with ethylene oxide). For comparison purposes, calculations were run for the detonation case, giving the detonation pressures, temperatures, and velocities, as a function of concentration. To provide a wide range of chemical reactivities, methane, propane, and ethylene oxide were used in these tests. For the deflagration tests, the reactivities were in the order methane less than propane less than ethylene oxide, and the fuel concentration was shown to be important. The spark source did not lead to immediate detonation, which was important because the low energy ignition hemisphere tests used the same type of spark source as the ignitor. The detonation results also showed a dependence on the fuel concentration. While the propane and ethylene oxide tests showed general agreement with the calculated values, the experimental methane

values were significantly below those calculated. Detonations were, however, shown to be possible and values for the detonation characteristics were established. Again, the reactivity was in the order of methane less than propane less than ethylene oxide. Tables 1 and 2 contain these results.

HEMISPHERE DETONATION TESTS

For the unconfined vapor cloud detonation field tests the cloud was simulated by inflating 5 m and 10 m radius thin walled polyethylene hemispheres with the desired fuel-air mixtures. The plastic material was sufficiently thin so as to cause minimum interference with the combustion ongoing inside. Stoichiometric or slightly rich fuel-air concentrations were always used. While the horizontal dimensions of accidental vapor clouds are typically much larger than the hemisphere diameters, 5 m and 10 m cloud heights are not unrealistic for clouds from liquefied gases. In all but the final test series, the hemisphere was inflated on a concrete test pad, equipped with an instrument channel containing a row of pressure transducers. High speed as well as real time photography provided additional data (Lind and Whitson, 1977).

In the first series of tests, low energy spark igniters (3 kV, 13.5 J) were used so that deflagrative flame velocities could be measured and the Deflagration to Detonation Transition (DDT) studied, if it did occur. Methane-air tests were performed three times, propane-air six times, ethylene oxide-air twice, ethylene once, acetylene twice, and butadiene once. In Table 3 are the results of this series. The six fuels were chosen so as to give a wide range of reactivity; although some reasonably high flame velocities were observed, there were no detonations and both the horizontal and vertical flame velocities became constant after the flame

front had moved away from the ignition point. The somewhat higher vertical velocities are probably due to buoyancy effects. The data gave no indication of even an incipient DDT. Since the passage of a flame front through a constriction or past a solid structure often results in a flame velocity increase, simple obstacles were added in test 6 and open tubes in test 2, but these failed to alter significantly the flame velocity. Partial confinement may be significant, however. The pressure transducers were arranged in a line along one axis on the floor of the concrete test pad. This required a partially covered instrumentation channel through which the flame front sometimes accelerated to a velocity that was somewhat higher than along the opposite radius. Even this velocity, however, was orders of magnitude below typical detonation velocities. Weak ignition did not seem to be a practical way to detonate liquefied gases; the deflagration velocities measured with methane-air showed that methane was the least reactive of the fuels tested with the exception of butadiene.

In the second series of hemisphere tests, Composition B, a high explosive, was used in attempts to directly initiate a vapor cloud detonation. Table 4 summarizes the eight tests. The first two involved stoichiometric methane-air mixtures in 5 m hemispheres mounted on the concrete pad. The methane used was commercial grade, about 96% pure, with 4% heavier hydrocarbons. High speed cameras, 8000 frames per second, and pressure transducers were used to monitor the experiment. The four pressure transducers were located 2.8 m, 3.4 m, 4.0 m, and

4.6 m from the exploding charge. The calculated maximum detonation pressure was 16.6 bars and the calculated maximum shock wave velocity was 1830 m/sec. Initiators of 1.35 kg, and 2.05 kg respectively, were used in these two tests, but the high explosive failed to cause the detonation of the fuel-air mixture, although a higher flame velocity was achieved. The plot of the pressure as a function of distance from the initiator produced the same curve as that of an explosion without the presence of a plastic hemisphere; the presence of the premixed fuel-air mixture did increase the pressures somewhat at each distance from the initiator. The pressure never exceeded 4 bars and the peak flame velocity was about 35 m/sec. Since unconfined vapor clouds composed of LPG have detonated after tank car and pipeline accidents, the next group of high explosive direct initiator tests involved the system methane-propane stoichiometric in air, always using a 1.35 kg Composition B initiator in a 5 m hemisphere. Test 20 was a calibration charge without fuel, with a maximum pressure of 4 bars. In tests 22-25, Commercial Grade methane was mixed with propane with test 21 being Chemically Pure Grade, about 99.9% methane. Usually the mixture of propane and heavier hydrocarbons was referred to as propane. The test series was run in the sequence 90% methane-10% propane, 57.6% - 42.4%, 76.8% -23.2%, 81.6%-18.4%, and 86.4% - 13.6%. Only methane concentrations above 81.6% failed to produce a vapor cloud detonation. The velocity of the fuel-air detonation wave was 1800 m/sec and the maximum pressure was 15.5 bars in the 81.6%-18.4% test. Clearly, for the 1.35 kg initiator, the critical percentage of propane for the methane-propane-air detonation is

between 13.6% and 18.4% propane; financial restrictions prevented the determination of critical concentrations for other initiator sizes. Theory suggests that the use of propane as a sensitizer is representative of all hydrocarbons heavier than methane. The 13.6% sensitizer concentration has special consideration as the commerical LNG being imported into the U.S. east coast has about 14% higher hydrocarbons.

Recent work by D. Bull and J. Martin of Thornton Research Laboratory (Bull and Martin, 1977) involved unconfined direct initiation of detonation in the system methane-oxygen-nitrogen, in which the oxygen-nitrogen ratio was greater than that occurring in air. Their extrapolation of the results of these direct initiation tests which used tetryl, a high explosive roughly similar in effect to Composition B, suggested that 22 kg of tetryl would directly initiate unconfined methane-air. Calculations by A. Boni of Science Applications, Inc. (Boni, 1978), predicted that larger quantities of initiator would be required, about 100-1000 Mg of tetryl. Whether the minimum direct initiation energy is 22 kg or 100 Mg is important because the latter would mean that accidental direct initiations of methane-air detonations are impossible. To distinguish between these two predictions a third series of two detonation tests was performed. Chemically Pure Grade methane was used which contained only about 0.1% impurities. Stoichiometric methane-air was used to inflate 10 m radius hemispheres. Charges of 22 kg and of 35 kg of Composition B were used. To avoid damaging the concrete pad used in previous tests, these were carried out on the desert

floor. High speed photography was used to monitor these tests and, to prevent the effects of the blast upon the sand from obscuring the tests, the high explosive was supported about 1 m above the ground. In neither case did the methane-air mixture detonate, with flame velocities and pressures continuing to decrease until the flame burned out. Since the high speed cameras were so successful in distinguishing between deflagration and detonation, the pressure transducers were dispensed with during the final two tests.

These series of hemisphere tests involved very weak ignitors and very strong ignitors. The weak ignitors were clearly not strong enough to achieve a DDT. Similarly, the strong ignitors may have been too strong for direct initiation - there has been speculation that high explosives are so energetic that they tear the fuel molecules apart with great violence. Perhaps an intermediate level of initiator might be more effective than either high energy explosives or low energy sparks. One way of producing this intermediate level of energy is to use a detonating wave front to initiate the methane-air mixture. If the wave front were methane-air, realism would be added as well. To achieve this in an experiment, a tube will be sunk into the desert floor, its mouth 0.6 m above the base of the hemisphere. Sheet explosive will produce a detonation wave in this partially confined geometry. Whether the confined planar detonation wave will undergo transition to a spherical detonation wave is the question. In many ways this series of experiments is more realistic than the high explosive series in that partially confined

spaces such as long, empty pipes and large and small buildings are present in port areas. These can fill with a flammable fuel-air mixture, ignite, and detonate due to the confinement; the practical question is whether the detonating methane-air mixture can propagate beyond the partial confinement.

Proving that the unconfined vapor cloud arising from an LNG spill can detonate under any circumstances is essentially impossible. The number of variables is very large, and the number of combinations is virtually infinite. If the intermediate initiator energy test does not result in a vapor cloud detonation, then high, medium, and low energy ignitors all will have failed to detonate the vapor cloud, and some conclusions can then be drawn about the likelihood of detonation. Clearly the influence of the fuel composition is significant in the tendency towards detonability. Small scale tests by R.C. Reid of the Massachusetts Institute of Technology have demonstrated that very significant component separation occurs when LNG is spilled onto water; whether this is the case in large scale spills was studied in the spill on water tests at the NWC. The results from the water spill tests indicated that while there was some selective boil-off, it was far from being as great as that found by Reid. The results suggest that real clouds would have significant quantities of higher molecular weight hydrocarbons in all parts of the vapor cloud if there were significant concentrations in the LNG. The completion of all detonation work is planned for July, 1979.

POOL AND CLOUD FIRES

Early in this study it became clear that vapor cloud deflagration was more likely after accidential spills of LNG on water than vapor cloud detonation; since immediate ignition of the spill was likely after a ship collision, pool fire was also worthy of study. Although diked LNG fires on land had been studied extensively prior to this time (for a review of past work, see Schneider, 1978), there had not been pool fire or cloud fire tests for LNG and for LPG. For comparison purposes, one gasoline pool fire test was run. A brackish, ground water-filled pond was excavated, 50 m by 50 m and about 1 m deep. The terrain was generally flat; control of the experiment was remote from a blockhouse 200 m from the pond. A polyurethane insulated cryogenic storage tank with a 8.0 m^3 capacity was connected to a pipe trestle leading to the center of the pond. Compressed nitrogen at 125 bars pressure, reduced to 3-6 bars pressure, provided the driving force for spilling the fuel through the 10 cm pipe. The pipeline diameter increased to 15 cm towards the discharge end and terminated in a 90% elbow, the fuel discharging vertically downwards about 1 m above the water surface. A circular metal plate just below the water surface served to spread the liquid outwards. Release rates ranged from 0.02 m^3/sec to 0.11 m^3/sec. The LNG and LPG were purchased from commerical sources, with assays performed prior to most cryogenic tests. The gasoline was commercial leaded motor fuel. Samples taken just before a spill test were analyzed by gas

chromatograph. All portions of the test equipment coming in contact with cryogens were designed and built according to current cryogenic industry standards.

The data collecting apparatus was extensive, and Table 5 summarizes the variety of equipment used. Both narrow-angle and wide-angle radiometers were used for measuring the thermal flux received at a distance from the fire; the former viewed only a portion of the flame, but the latter viewed the entire fire. In tests LNG 12-17, sapphire and zinc selenide windows were used. The radiometry data were recorded on magnetic tape. In the test LNG 5, a pool fire, an infrared spectrometer was used to evaluate the actual emission spectrum, determine the flame temperature, and estimate the emissive power. In the test LNG 12, a pool fire, 5 cm by 5 cm fir wood stakes were driven into the pond to provide an estimate of the thermal flux based on the location of the charred wood samples. Several cameras provided a permanent record of each test, and flame dimensions and flame speeds were calculated from these films. A minimum of three 16 mm cameras was used, one aligned with the wind, one crosswind, and one overhead, the last suspended from two tall polls at a height of 45 m and about 120 m from the spill point. Usually camera speeds were 100 frames/sec, but sometimes a speed of 24 frames/sec was used. Additional records were provided by a 70 mm still camera in six of the last ten tests. In several early vapor cloud tests a thermal imaging camera was used to locate the methane cloud; the visible portion of the cloud was water vapor. An improved version of

this infrared camera was used in the vapor dispersion tests LNG 18, 20, and 21. Operational decisions during each test were aided by the use of closed circuit television; no videotape record was made. In tests LNG 1-11, wind speed and direction were recorded at two locations, in the area of the command bunker and 10 m upwind of the pond. In tests LNG 12-21, there was only one station. Hydrocarbon concentration sensing in most of the vapor fire and vapor dispersion tests was achieved using five evacuated gas sample bottles located in the pond, remotely opened and closed to take vapor samples at various times. In test LNG 1, some 29 thermocouples were placed on the water surface and at various depths near the spill point, with the aim of measuring the temperature profile under the cryogen pool; data were recorded on a 30 channel data logger manufactured by Datum, Inc. The test site was provided with several markers for use in pool fires to measure flame dimensions, in the vapor cloud fires to aid in the determination of flame dimensions and flame speeds, and in the vapor dispersion tests to measure the cloud dimensions. Two markers were provided for each camera, perpendicular to the camera line of sight and aligned with the spill point. In the later tests LNG 12-21, additional markers were deployed to facilitate measurements.

In general, there were few technical difficulties with the spill procedure or the execution of the fire tests. Extreme caution was taken due to the hazards of these tests. There were difficulties with the radiometers but these were later resolved. The simplicity of the wood

stakes, markers, closed circuit television, movie cameras, and the still camera insured their success. The spectrometer and the thermal imaging camera also presented no problems. The data logger and the wind speed and direction devices functioned without difficulty. The thermocouples demonstrated that below a few centimenters from the surface no significant cooling occurred, so the shallow, 1 m depth of the pond did not affect the results. Agitation of the water surface due to the violent boiling of the cryogen prevented the thermocouples located near the water surface from giving any useful information. The gas sample bottles showed enrichment in methane concentration relative to the LNG assay in the early stages of pool boiling; some pond water did enter the bottles due to surface agitation. Towards the end of pool boiling, the concentration of methane fell beneath that in the assay. Evidently the boiling process did provide a degree of separation, but not a total one. Above all, the emphasis on safety insured that no injuries occurred and no major damage occurred to the instrumentation.

Both pool fire tests and cloud fire tests were run with LNG and with LPG. For comparison purposes, a single gasoline pool fire test was performed. Essentially, the difference between a pool fire and a cloud fire was determined by the time and the location of the ignition, with ignition by two or more electrically operated flares. The pool fires were ignited by two flares near the spill point, ignition being simultaneous with the start of the spill. In three cases, ignition was delayed to permit the LNG pool to spread out and then, after ignition, to have a larger pool

fire, perhaps one that would be optically thick. In test LNG 7, the first of the delayed ignition tests, the flame failed to spread quickly throughout the LNG, so in the later two tests LNG 13 and 14 a circular array of five flares was used, and a larger diameter pool fire was achieved, but the entire pool did not quickly ignite. The cloud fires were ignited by the flares some distance downwind on the land. Qualitatively, the pool fire was very tall for its diameter with a very clean LNG flame until, near the end of the fires, some smoke appeared. The LPG fire was very smoky throughout the burning period and the gasoline fire even more so. The LNG cloud fire was so clean that the flame front was difficult to discern; the LPG fire was smokier. Curiously, the cloud fire tended to stall for a time on the land side of the pond's edge; after a delay during which the cryogen almost totally evaporated, the fire spread into the pool. The flame velocities were not high nor did they show any indication of acceleration. At the end of the LNG and LPG spill tests there was always an ice-like solid that burned at the end of the tests, and that was gone before samples could be taken. Long depth of focus films showed the surfaces of this material to be uneven and similar to ice in appearance. The difficulties involved in the safe sampling of the material while avoiding contaminating or melting the ice-like material prevented any further characterization. Finally, the thermal imaging camera showed that the methane cloud extended beyond the visible cloud.

The major objective in these tests was to prepare a model for LNG and LPG fires. At the time of this writing, the data from the LPG and the gasoline fires had not been processed. In order to prepare a model for LNG pool fires, several parameters must be known quantitatively. These include the pool/flame diameter, the LNG vaporization rate, the flame height, and the thermal emissive power. Since the LNG pool/flame cylinder maintained a constant diameter during the spill period, and assuming that the spill rate remained constant, a steady liquid regression rate could be calculated from the films of the fires. This rate ranged from 4×10^{-4} m/sec with a tendency for higher regression rate with the higher spill rates; this trend could be due to greater fragmentation of the LNG when the faster streams of LNG strike the water. Flame heights peaked as much as six times the flame diameter. The Thomas correlation served reasonably well as an estimator of the pool flame height; since the flame heights did vary by as much as 10 m during some experiments (with average heights of 25 m to 55 m), there is some uncertainty. The thermal emissive power was of the order of 210 to 220 kW/m^2. The narrow angle radiometers gave a figure of 210 ± 20 kW/m^2 and the wide angle radiometers 220 ± 50 kW/m^2. In one test, the wood sample charring results led to an estimate of 185 kW/m^2. The spectroscopic data lead to a value of 210 kW/m^2. The spectrometer gave additional results - the thermal radiation was mainly in the carbon dioxide and water bands, with some radiation from luminous soot, confirming the visual evidence of a clean fire. The flame had a temperature of 1500K; had the fire radiation been black body radiation at

1500K, the thermal emissive power would have been about 290 kW/m^2. Since the radiation is largely in the carbon dioxide and water bands, these gases in the atmosphere will absorb some of the radiation, reducing the effects of an LNG pool fire more rapidly than had it been a petroleum fire. Also mitigating the effects of an LNG fire was the fact that the fraction of combustion energy released in the form of radiation fell from 32% to 12% as the spill rate increased, perhaps due to a mixing of the products of combustion with the unburned core preventing all of the fuel from burning. Qualitatively, there were no marked differences between the radiation from an immediate ignition and the delayed ignition pool fires. Ignition of the entire pool was very slow in these tests; in LNG 13 and 14, despite the five ignition points, there was a significant delay before the entire pool ignited. Apparently, only after vaporization was essentially complete did the total pool burn. Finally, there was no evidence of the fireball type of burning.

The vapor cloud fire results also were used to model the LNG fires. The important parameters are the flame speed, the flame length, and the thermal emissive power. Both the flame speed and flame height were measured from the motion picture film. The clean burning nature of the flame produced some uncertainty in the exact location of the flame. The flame speed increased with the wind speed, with flame velocities of up to 17 m/sec, higher than the flame speeds in the weak initiator hemisphere tests; this may have been due to the turbulence-increasing effects of the terrain. While the premixed flame measured in the

nightime test, LNG 16, did burn faster than the diffusion flame, the portion of the cloud that was premixed was so small that little error was introduced by using the diffusion flame speed only. The length of the flame as measured from the base to the top of the flame ranged from 10 m to 30 m. The ratio of the length of the flame to its width averaged 0.5, so the use of a ratio of 1.0 is a conservative value. The thermal emissive power measured by the narrow angle radiometer was 220 ± 30 kW/m^2 while the wide angle radiometers gave a figure of 200 ± 90 kW/m^2. An optically thick flame at a temperature of 1500K would give a thermal emissive power within the upper range of the radiometer data. No fireball behavior was observed; at no time did the burning cloud appear to rise from the surface, even when it was stalled at the pond edge.

Therefore, the average thermal emissive power in all of the LNG tests was about 220 kW/m^2, the equivalent of 70,000 Btu/hr ft^2, about twice that in conventional petroleum fires used for such design purposes as sizing safety relief devices. This excess may be less important than it appears, however, because of greater atmospheric absorption than with petroleum fires. Also, there were no signs of flame accelerations in the vapor cloud fires and no evidence of fireball behavior in either the pool fires or cloud fires; both flame accelerations and fireballs would have significantly increased the hazards of LNG fires.

As mentioned previously, the LPG and gasoline test results have not been evaluated as yet. There were, however, no apparent problems

with the four LPG immediate ignition pool fires, the four LPG cloud fires, and the one gasoline immediate pool fire. Table 7 presents some data on these fire tests. Generally, the same instrumentation was used in the LNG spills, although some instruments were relocated to account for the change in fuels. Assays were performed on the LPG prior to the tests LPG 1,3,4, and 5 but, due to the very minor variation in composition with time and the short period between tests (eight LPG tests over a ten day period compared with the first eleven LNG tests over a ten month period), the other assays were deemed unnecessary. Note that this type of LPG was very rich in propane. Analysis of the raw test data should present few problems, but the development of models for LPG and gasoline fires similar to those for LNG may be difficult due to the soot that was present; the obscuring soot may prevent accurate measurement of the LPG and gasoline flames.

In this series of LNG, LPG, and gasoline pool and cloud fires, only diffusive burning was observed. No flame front accelerations were noted in the vapor cloud tests; fluxes were greater than expected for all types of LNG tests; and the delayed ignition LNG pool fire tests showed the difficulties of the rapid, total ignition of a large spill; in sum, the fires were less "violent" than previously thought by many. At no time was there any evidence of a tendency to detonate or to burn as a fireball; simple diffusive burning can model these events.

DISPERSION TESTS

The United States Department of Energy (DOE) has published plans for an extensive program of LNG research, including large scale LNG spills (Department of Energy, 1978), and the U.S. Coast Guard has managed a portion of the preliminary DOE work as a part of the ongoing China Lake program. One major prerequisite for the 40 m^3 spills scheduled by DOE is a good understanding of the downwind vapor cloud shape so that gas detectors can be properly located. Another requirement is the development of improved gas sensing instrumentation, particularly instrumentation that can distinguish between methane, ethane, propane, and butane. Four vapor dispersion tests were performed, LNG 18-21, identical to the vapor cloud fire tests except that no ignition occurred (Department of Energy, 1979). Table 8 gives some of the tests details. For a definition of the cloud shape an array of cameras (including a thermal imaging camera), thermocouples, and Mine Safety Appliances (MSA) Combustible Gas Detectors was deployed. In theory, if the mixing of the LNG vapor with air is adiabatic, the temperature at each point in the cloud can be converted into a point concentration. Some 29 Chromel-Alumel thermocouples were arrayed downwind from the spill point to test this theory. The MSA sensor was a passive device using two heated filaments; the flammable gas-air mixture is oxidized by the catalyst-coated filament, while the other filament is inert. The difference between the heat transfer rates from the heated filaments

can be related to the fuel-air concentration. The MSA devices were inexpensive, proven, reliable, and rugged; 15 were arrayed downwind of the spill point. These instruments, however, were limited by an inability to detect separately the constituents of the vapor cloud, a slow response time, and an inability to measure vapor concentrations above the stoichiometric. The characteristics of the 'perfect' gas sensor include that it be rugged, reliable, inexpensive, have a rapid response time, cover the entire concentration range, and have an ability to distinguish between the components of the vapor cloud.

Several candidate instruments have been developed by the Coast Guard and other organizations. Note that the development of the instruments from the Jet Propulsion Laboratory was funded by the Coast Guard; the other five instruments were either developed or procured by the DOE. Table 8 describes the instruments that were tested in the vapor dispersion tests.

In addition to the thermocouples and the MSA devices, seven other instruments were tested. The Shell device, built by Shell Research Ltd, is a forced-flow version of the MSA detector. It can, however, detect hydrocarbon concentrations up to 100%. The TSI device, manufactured by Thermo-Systems Inc., measures the sonic flow velocity through an orifice using two thin film anemometers. Since the sonic velocity is a function of the fuel composition and temperature, the hydrocarbon concentration can be calculated after correcting for the temperature

variations. The Anarad IR detector, custom built by Anarad, Inc., is a non-dispersive IR analyzer that is basically composed of three infrared spectrometers, which together are able to measure the methane, ethane, and propane concentrations. The LLL IR detector, built by Lawrence Livermore Laboratory, is a conversion of a rapid response carbon dioxide detector to sense hydrocarbons. Although it can not separate the hydrocarbons, modification of the two filter system (one hydrocarbon, one reference) to a five filter system would permit the separate detection of methane, ethane, and propane. The presence of water vapor, water droplets, and dust does not interfere with measurements. The CGC LIDAR, custom built by Computer Genetics Corporation, is a laser Raman (emission rather than absorption) system. The instrument tested must be used at night, but this limitation could be removed, as could its inability to distinguish between the hydrocarbons; however, there is no way to see into or through the LNG-produced water fog. Since the flammable region extends beyond the visible fog, the LIDAR device is potentially useful; furthermore, the LIDAR is the only device that averages the concentration over a long distance, of the order of 45 m in this case. The JPL laser, developed by the Jet Propulsion Laboratory, is a helium-neon laser instrument, producing two beams of differing wavelength, one absorbed by methane and one not. In this way only methane is detected. As constructed, the laser system had two sensors for measuring methane concentration, so that although it was only one instrument, it measured the gas at 1.5 m and 2.5 m above ground level. The Two-Band Differential Radiometer (TBDR), also developed by

JPL, is based on the principle that the difference between the absorption of methane at 2.1 um and 2.3 um can be used to determine the methane concentration. Broadband radiation from a thermal source is used rather than narrow band radiation. To validate the seven instruments, the MSA detectors, and the thermocouples, Grab Samplers, designed by Lawrence Livermore Laboratories, were provided at eight instrument stations. These were evaculated bottles with solenoid-actuated valves and were somewhat more complex than the sample bottles used in the cloud fire tests. Note that the type of sample bottles used in some earlier fire tests was not deployed in these dispersion tests. The added complexity in the LLL Grab Samplers was the addition of a warming tube in the inlet to the sample bottles. Analysis of the sampled gas was by mass spectrometry.

All devices were used in tests LNG 18-21, except for the CGC LIDAR, used only in the nightime test, LNG 19. The MSA sensors were arrayed in a grid formation at twelve locations. The seven types of instruments being evaluated were deployed at nine stations. The instruments in the latter array are described in Table 8. Despite changes in the wind direction and occasional instrument malfunctions during the four LNG spill tests, each instrument had at least one successful test. Long delays due to undesirable wind conditions meant that the evaluation of these detectors is incomplete at this time; current plans are to select perhaps half for further evaluation during the planned DOE 40 m^3 tests. Some general comments are possible. The thermocouples gave good

results near the spill point but the agreement with the MSA detectors was not as good further downwind, suggesting that there was some warming of the vapor cloud by means other than adiabatic mixing with air. This warming, if true, might tend to mitigate the long downwind dispersion distances predicted by some, most of whom have assumed an absence of warming. The MSA sensors presented no difficulties. The Shell and TSI detectors showed good agreement with nearby Grab Samplers. The Anarad IR detector proved fragile in transportation, though not in use, and some signal "cross-talk" between the methane, ethane, and propane channels reduced the accuracy of the instrument. It was concluded that major changes would be required before this device could be used in field experiments. The LLL IR detector showed fairly good agreement with the adjacent Grab Sampler. The CGC LIDAR results could not be directly compared with those from the Grab Samplers due to the spatial averaging of the LIDAR and the fact that most of the detectors in the pond were 2 m or more below the LIDAR laser beam; the LIDAR results were at least qualitatively reasonable and the device was considered to have shown some promise. The JPL laser and the JPL TBDR detectors agreed with one another; Grab Samplers were not located nearby for comparison purposes. Thermister temperature results at the same location showed agreement with the TBDR, assuming that the vapor cloud warms only through adiabatic mixing with air. The Coast Guard is continuing the development of the TBDR. Finally, the Grab Samplers performed well.

The LNG dispersion test showed the general shape of the LNG vapor cloud - the visible cloud did show agreement with the sensors. The tests also provided a preliminary evaluation of seven gas detectors for use during future tests. The performance of six of the seven detectors was promising, and even the seventh could be redesigned for further evaluation. Nevertheless much work is needed before the "perfect" detector can be built.

JET PROPULSION LABORATORY SENSORS

Along with managing the four LNG dispersion tests used to evaluated the nine types of gas sensors, the Coast Guard sponsored the development of two of the sensors, the JPL laser and the Two-Band Differential Radiometer (TBDR). Both the National Aeronautics and Space Administration and the American Gas Association provided financial assistance. The goal was to develop an instrument capable of rapidly responding to the fluctuating hydrocarbon concentration.

The JPL laser is a single frequency helium-neon device that measures the infrared (IR) absorbtion peaking at around 3.39 um. This laser system was chosen due to the very short 2 cm optical pathlength required and to the fact that few other chemicals absorb near this wavelength. Sources of error include water vapor absorption near 3.39 um, temperature variations affecting measured values, and laser noise. None of these proved to be major problems. The laser device, in field use, consisted of two sensors 1.5 m and 2.5 m above ground level, a mechanical chopper, a single laser, InAs infrared detectors, and several thermisters, some located near the sensors. By using an air conditioner prior to each field test, the instrument's temperature was sufficiently constant during the test to achieve accurate measurements.

The JPL TBDR is a more complex instrument. By measuring the absorption of two wavelengths of light, one wavelength that is strongly absorbed by methane and one which is not significantly absorbed, the concentration of methane can be accurately measured. This is true, however, only if the other gases present do not also absorb preferentially, that any particles present do not strongly reduce the amount of radiation transmitted, and that any particles present absorb and scatter the same proportion of radiation at each wave-length. A nonlaser, broadband light passes through a 15 cm long gas sample and then is split into two beams. By using a filter transmitting light at only 2.1 um in line with one beam, and a filter transmitting light at 2.3 um in line with the other beam, with sensors for each filtered beam, the 2.3 um light beam is partially absorbed by the hydrocarbons but not by oxygen, carbon dioxide, nitrogen, or water vapor.

One two-sensor laser device and two identical TBDRs were tested at China Lake during the dispersion tests LNG 18-20; one TBDR and the laser were tested during LNG-21. Both types of detectors were built, tested, and calibrated at JPL. The instrument station was located 55 m away from the spill point. The TBDRs were located 0.5 m above the ground close to the laser device, with the laser's sensors 1.5 m and 2.5 m above the ground. In test LNG 20 the cloud completely missed the detectors; in test LNG 19, the cloud reached the sensor for only very limited periods; in tests LNG 18 and 21, the cloud covered the sensors for

a long period and good data were obtained. The data from tests LNG 18 showed excellent agreement between the laser sensors and the TBDR, and between the laser and the TSI device, which was located at the same distance from the spill point. Only short puffs of cloud reached the JPL station during test LNG 19. There was agreement between the two laser sensors and one TBDR (the other malfunctioned) as to the time of arrival of the cloud puffs. More significant were the results of test LNG 21. The TBDR that was used was located within 20 cm of the lower laser sensor, as was a thermister. Some 70 seconds of data were recorded. The temperature profile showed qualitative agreement with the TBDR and the lower laser sensor output. There was qualitative agreement between the laser and TBDR measured concentrations.

The results of these tests indicate that the laser and TBDR devices are promising and that, with further development, both probably would make a contribution to LNG research. The thermister results suggest that the cloud temperature shows promise as a measurement of concentration, but again further work is needed. Thermisters have excellent properties - inexpensive, simple, rugged, rapid response and small sample volume; no distinction is possible, though, between the various hydrocarbon species.

Two additional instruments were studied at JPL. One was the design of an oxygen detector, with the goal of being able to measure not just the fuel in a vapor cloud but also the oxidizer. The detector built

used ultraviolet (UV) absorption in the 0.1923 - 0.1947 um range where hydrocarbons do not absorb. The device as designed included a deuterium lamp as the UV light source, quartz windows, a 1 m long sample cell, and a monochromater. A photomultiplier served to measure the transmitted light. Since water vapor absorbs in these wavelengths, a second beam is required at either 1.4 um or 2.7 um in the infrared range. The investigators at JPL felt that the proposed system design would work successfully. The second area of laboratory work was in infrared fiber optics research. The principle objective was to develop a liquidfilled quartz fiber that could transmit radiation with acceptably low losses. Carbon tetrachloride was determined to be the optimum choice, and the loss per meter was measured.

The Coast Guard is concentrating its efforts in the development of a Four-Band Differential Radiometer (FBDR), capable of measuring methane, ethane, and propane concentrations separately. The laser development was terminated not due to poor performance during the dispersion tests but due to the fact that the Department of Energy's Lawrence Livermore Laboratory laser detector is undergoing further development, and that only limited funds are available to the Coast Guard. The FBDR will probably be tested in the scheduled 40 m^3 DOE spill tests.

WIND TUNNEL TESTS

The United States Coast Guard, with the support of the American Gas Association and the Gas Research Institute, has funded a feasibility study of using wind tunnels to simulate the China Lake spills. Prof. Robert N. Meroney of the Colorado State University (CSU) is performing this study. This effort was preceeded by one supported by the AGA through R&D Associates, Project IS-128-1. There are two reasons for conducting wind tunnel simulations: LNG spills are extremely expensive, limiting the number of tests; and the spill conditions are not easily changed, limiting the number of variations possible. The objective of the study was not to replace field tests with wind tunnel tests but to determine whether the wind tunnel tests could replicate the field test results. Once there is evidence of good agreement with past field tests, variations in spill conditions would then be possible. This is where the flexibility of the wind tunnel becomes so valuable; for example, very stable weather conditions do not exist at China Lake, but commonly do exist at night over water. Also, wind tunnel tests would be useful in planning the larger LNG spills - these tests could determine the optimum location for the LNG sensor equipment, for example. Wind tunnel tests can not completely replace field tests, because the fundamentals of LNG spills are not completely understood; rather, until the travel and dispersion of a vapor cloud are better understood, wind tunnel tests should be considered only a potentially valuable adjunct to field tests.

Most of the CSU work has been completed but no report is available at this time. There were two CSU wind tunnels used, the Meteorological Wind Tunnel (MWT) and the Environmental Wind Tunnel (EWT). In principle, to model the atmospheric boundary layer, that is, the first 1000 m of the atmosphere, a scale of 1:170 is required. Due to the low-lying nature of the LNG vapor cloud, a larger scale of 1:85 was possible, permitting better resolution of the dispersion phenomena. The method used by Meroney to obtain scaling parameters was that of similitude, that is, by developing mass ratios, force ratios, energy ratios, and property ratios. For example, the mass ratio was defined as the mass flow of the cloud divided by the mass flow of the air, and the volume flux ratio was defined as the volume flow rate of the cloud divided by the volume flow rate of the air. To be sure, it is not possible to scale all properties at the same time; the best that is possible is to scale those parameters determined to be important.

The LNG was simulated by argon. Since the adiabatic cloud mixing model was chosen as being the most conservative, and the variation of cloud density with mole fraction in air was an important parameter, argon was used since it had a density variation similar to that of air. Perhaps most importantly, argon is inert and easily measured. The wind velocities were scaled properly and the Froude Number was simulated over the region of interest. The LNG experimental boiloff rate varied in an uneven manner that was not really well known, so the argon was released at a constant rate.

The MWT is 1.83 m in width and the EWT is 3.66 m in width. Thermal stratification was produced by heating and cooling systems in the wind tunnel. Wind velocities of 0.3 to 24 m/sec are possible in the MWT and 0.15 to 12 m/sec in the EWT. Vortex generators were installed to provide the boundary layers with an initial impulse. The EWT is larger than the MWT and both have adjustable ceilings to vary pressures and long test sections to allow the development of the dispersion phenomena.

Argon was released from a high pressure cylinder through a reducing valve into a simulated area source. Smoke was produced to define the cloud by passing the argon through titanium tetrachloride. Still photographs were taken with a Polariod Camera and a 35 mm camera, and motion pictures were taken as well. Wind velocities and velocity profiles were measured with anemometers and hot probes. Concentration measurements were made with hot film aspirating probes, having something in common with the MSA sensors in that a change in heat transfer from a hot film surrounding a hot, electrically heated wire can be correlated with composition. A vacuum pulled the argon-air mixture past the wire. The sample area of this device's inlet probe was 1.88 cm^2 corresponding to a sample area in the field of 1.6 m^2, much larger than the sensors - save the Raman LIDAR - during the dispersion tests LNG 18-21.

There were seventeen wind tunnel tests, divided into four groups. The purposes of these tests included the evaluation of the test system,

comparison of the 1.170 and 1:85 scales, the effects of changing cloud's specific gravity, comparing the effects of smooth floors with China Lake topography, measuring the horizontal and vertical velocity fluctuations, and simulating the field tests LNG 18-21. In the first group of tests, five 1:170 5.95 m^3 spills with a spill rate of 0.079 m^3/sec were performed; two wind speeds and three wind directions were used. Very low wind speeds (2.2 m/sec) showed instabilities in the wind tunnel. This first group of tests was in the MWT; the remaining three groups of tests were in the EWT. In the second group of tests, four 1:85 5.95 m^3 spills at a spill rate of 0.079 m^3/sec and at two different wind speeds were performed. Comparison of the first two groups of tests showed no effect of scale on concentration measurements. In the third group of tests, two were performed with China Lake topography and two without; two sets of spill conditions were used, one of each set in the two tests with China Lake topography and one of each set without the topography. The presence of topography made a great difference, with more dispersion in the topography tests. Longitudinal and vertical velocity fluctuations were measured. Finally, the fourth group of tests simulated LNG 18-21. The agreement between the NWC grid of MSA sensors was poor, with some peak concentrations measuring several percent while the model reported 0%. In other locations, the peak model concentration was as high as 10.8% while the field reported 0% at the same location. Although concentrations were not measured at wind tunnel locations corresponding to the sensor locations on the LLL grid, interpolation permitted estimates of the concentration at points on the model corresponding to the

exact location of the sensors on the LLL grid. At some locations, agreement was better than with the NWC grid, but there were still locations showing poor agreement. The best LLL agreement was during simulation of test LNG 21 .

In this simulation program, the results show that, at the least, wind tunnel modeling is feasible. The level of agreement between the model and field tests indicates that more work is needed before placing great confidence in wind tunnel modeling. The agreement was sufficient to warrant further research, considering the huge costs involved with field tests and the constraints on the experimental conditions at the test site. The Gas Research Institute is continuing research at Colorado State University in this area.

CONCLUSION

The U.S. Coast Guard's research program at the Naval Weapons Center, China Lake, California, and related projects, has proven very productive in increasing our understanding of the behavior of large releases of LNG, LPG, and other similar liquefied gases. While this program is not yet complete, some conclusions are possible. A theoretical model, and deflagration and detonation tests in confined spaces provided guidance for the later tests. Methane-air mixtures are very difficult to detonate, perhaps impossibly so; even large quantitities of high explosive have failed to ignite directly to detonation. Relatively small amounts of propane, however, serve to sensitize the methane to detonation. In the absence of high energy initiators, no high flame speeds or overpressures will occcur. Both pool and cloud fires of LNG and LPG showed that neither fireball burning nor detonations are very likely. Models for LNG pool and cloud fires were developed, with the very high thermal flux of over 210 kW/m^2 for both types of burning. The boiling process did, to a minor degree, separate the components of LNG. The development of two Coast Guard hydrocarbon vapor sensors at the Jet Propulsion Laboratory was successful and one is undergoing further development for separately measuring the concentrations of methane, ethane, and propane. Seven additional Department of Energy sensors were evaluated during LNG vapor dispersion tests. Wind tunnel simulation of the China Lake Spills showed some promise. The Coast Guard has found this program helpful in fulfilling its regulatory duties.

Where does the Coast Guard's research go from here? There are many chemicals being shipped today. Enough is now known about LNG, LPG, and other similar liquefied gases to permit a refocussing of the Coast Guard's efforts. Currently, sulfuric acid spills are being studied in the laboratory, soon to be followed by field tests. Before the end of 1979, large spills of liquefied ammonia on both land and water will be conducted at China Lake. The Department of Energy will be the primary force in LNG and LPG research over the next few years. Throughout this research, the goal is the same: protecting the lives and property of the American people by minimizing the risks associated with the transportation of hazardous materials.

Table I

Shock Tube Tests: Measured Deflagration Properties

Fuel	Concentration volume %	Velocity m/s	Pressure bar
Methane	8.0	45	0.014
	9.0	63	0.019
	9.5	58	0.019
	10.0	55	0.026
Propane	4.0	128	0.034
	5.0	91	0.033
Ethylene oxide	6.0	116	0.061
	7.0	233	0.110
	7.5	270	0.120
	8.0	130	0.076

Fuel	Concentration	Experimental		Calculated	
		Pressure	Velocity	Pressure	Velocity
	volume %	bar	m/s	bar	m/s
Methane					
(90 g booster)	5.0	5.4	950	11.2	1490
	6.0	5.6	950	12.6	1590
	7.0	6.5	1010	14.0	1675
	8.0	5.4	1030	15.2	1730
	9.0	7.0	1030	16.0	1780
	10.0	7.8	1050	16.5	1820
	11.0	7.1	950	16.6	1830
	12.0	6.6	910	16.4	1820
Propane					
(90 g booster)	3.0	13.7	1710	15.2	1675
	3.6	15.2	1800	16.6	1750
Ethylene oxide					
(5 g booster)	5.4	15.5	1770	15.5	1700
	9.7	17.0	1840	19.6	1880
	19.9	19.5	1810	19.9	1900

Table 3

Low Energy Ignitor Hemisphere Tests

Test No	Fuel	Concentration Volume %	Size Diam m	Horizontal Velocity m/sec	Vertical Velocity m/sec at 3 m	Velocity m/sec at 8 m
1	Propane	4.0	5	A	6.3	-
2	Propane	5.0	5	B		
3	Propane	5.0	5	C	7.4	-
4	Propane	5.0	5	8.3	10.2	-
5	Methane	10.0	5	5.8	7.3	-
6	Propane	5.0	5	6.9	9.5	-
7	Methane	10.0	5	C	7.3	-
8	Ethylene Oxide	7.7	10	14.7	16.0	22.4
9	Ethylene Oxide	7.7	10	D		
10	Ethylene Oxide	7.7	10	13.4	15.2	22.5
11	Propane	5.0	10	9.6	9.9	12.6
12	Propane	4.0	10	6.1	7.8	10.6
13	Methane	10.0	10	5.2	6.5	8.9
14	Ethylene	6.5	5	8.8	17.3	-
15	Acetylene	3.5	5	3.6	4.6	-
16	Methane	10.0	5	E		
17	Butadiene	3.5	5	3.9	5.5	-
18	Acetylene	7.7	5	23.7	35.4	-
19	Methane	10.0	5	E		

Notes:

A. This test was carried out in the daylight and only the top of the flame was visible. Therefore only a vertical velocity could be measured.

B. This test ignited prematurely, and no data were recorded.

C. The fuel in the instrument channel burned, distorting the flame shape, so that only a vertical velocity could be measured.

D. Due to an instrumentation malfunction, no data were recorded.

E. These were detonation tests and are described in Table 4.

Table 4

High Energy Ignitor Hemisphere Test

Test Number	Fuel % Methane	Fuel % Propane and heavier	Hemisphere Diameter m	Initiator Size Kg	Detonation
16	96.	4.	5	1.35	No
19	96.	4.	5	2.05	No
20	0.	0.	Note 1	1.35	Note 1
21	90.	10.	5	1.35	No
22	57.6	42.4	5	1.35	Yes
23	76.8	23.2	5	1.35	Yes
24	81.6	18.4	5	1.35	Yes
25	86.4	13.6	5	1.35	No
26	100.	0.	10	22.	No
27	100.	0.	10	35.	No

Note 1. This test was run to determine the pressure profile produced by the high explosive charge; no hemisphere or fuel-air mixture was present.

Table 5

Details of Spill Tests LNG 1-21

No	Type	Vol m^3	Spill Rate m^3/sec	Wind Speed m/sec	LNG Compostion, Volume % Methane	Ethane	Propane	Higher Hydrocarbon
1	Pool	5.3	0.02	2.1				
2	Pool	5.3	0.10	3.1				
3	Pool	4.2	0.09	1.0				
4	Pool	4.2	0.02	1.5	75.6	19.0	3.9	1.6
5	Pool	3.0	0.09	0.0	75.4	19.4	3.9	1.3
6	Pool	5.7	0.11	3.1	75.6	17.8	5.0	1.7
7	Delayed	5.7	0.08	1.5	66.9	14.7	3.0	3.8
8	Vapor	5.1	0.06	4.1				
9	Vapor	5.3	0.07	7.2	95.1	1.8	1.7	0.7
10	Vapor	4.9	0.07	4.1	93.8	5.3	0.8	trace
11	Vapor	5.2	0.08	4.1				
12	Pool	5.4	0.07	0.0	88.0	9.6	2.06	0.25
13	Delayed	5.7	0.06	2.1	79.2	13.1	4.27	2.10
14	Delayed	5.5	0.07	0.0	94.9	3.8	1.18	0.19
15	Vapor	5.0	0.07					
16	Vapor	4.4	0.06	7.2	95.6	3.4	0.71	0.22
17	Vapor	5.5	0.07	7.2	94.1	5.1	0.71	0.09
18	Dispersion	4.4	0.07	6.2	94.2	4.4	1.10	0.31
19	Dispersion	4.5	0.08	5.1	95.0	3.9	0.75	0.30
20	Dispersion	4.5	0.06	11.3	91.4	8.1	0.33	0.14
21	Dispersion	4.2	0.08	4.6	92.7	4.5	2.31	0.46

Table 6

Spill Test Instrumentation LNG 1-21

Number Used	Instrument	Tests Used	Comments
2	Narrow Angle Radiometers	LNG 1-18	7^{o} Full cone
4(LNG 1-11) 5(LNG 12-17)	Wide Angle Radiometers	LNG 1-18	150^{o} with Bezel windows, 180^{o} without windows
1	Data Logger	LNG 1-18	For all radiometer data
1	Spectrometer	LNG 5	Infrared 1.5 um - 5.5 um
8	Wood Stakes	LNG-12,13	Fir, 5 cm by 5 cm, extending 0.5 m above the water
3(LNG 1-16) 5(LNG 17)	Movie Cameras	LNG 1-18	Usually 100 frames/sec One crosswind, one overhead, one with the wind
1	Still Camera	LNG 13-14	70 mm
1	Thermal Imaging Camera	LNG 7,18, 20,21	Improved version used in LNG 18,20,21

1	Closed circuit Television	LNG 1-21	
2	Wind speed and direction stations	LNG 1-21	One at bunker, one 10 m upwind of pond
5	Hydrocarbon Sensors	LNG 8-11 16-17	
29	Thermocouples	LNG 1	
Varied	Markers	LNG 1-21	

Table 7

Details of Spill Tests LPG 1-8 and GAS-1

LPG	Type	Volume m^3	Spill Rate m^3/sec	Wind m/sec	Ethane %	Propylene %	Propane %	Butane %
1	Pool	5.3	0.08	0.0	3.4	2.7	92.7	1.2
2	Cloud	5.8	0.09	3.1				
3	Pool	4.8	0.06	1.5	0.5	2.3	93.5	3.4
4	Pool	5.1	0.09	1.0	Trace	2.6	94.1	2.6
5	Pool	5.5	0.10	2.6	Trace	3.1	94.4	1.6
6	Cloud	4.5	0.07	5.1				
7	Cloud	5.8	0.09	5.1				
8	Cloud	5.8	0.10	3.1				
Gasoline								
1	Pool	6.8	0.06	1.5				

Note: 1. All LPG assays showed a trace of higher hydrocarbons.

2. No assays were performed for LPG-2, 6, 7, 8, and GAS-1.

Table 8

Some Characteristics of the Sensor Instrumentation

Tests LNG 18-21

Instrument	Response Time Sec	Sensitivity	Range	Status	Capability
Thermocouples			0-100%	Proven	Hydrocarbons
MSA Detector	Several		0-10%	Commercial	Hydrocarbons
Shell Detector	0.7		0-100%	On Loan	Hydrocarbons
TSI Detector	0.010		0-100%	Commercial	Hydrocarbons
Anarad Detector	Several		0-100%	Commercial	Meth.,eth.,pro.
LLL IR Detector			0-100%	Custom Built	Hydrocarbons
CGC LIDAR			0-100%	Existing Device	Hydrocarbons
JPL Laser	0.005	0.1%	0-100%	Custom Built	Methane
JPL TBDR	0.15	1%	0-100%	Custom Built	Methane
Grab Sampler	N. A.		0-100%	Custom Built	Complete Separation

Table 9

Location of Instrumentation During Tests LNG 18-21

Instrument Station		1	2	3	4	5	6	7	8	9
Instrument	Total									
Thermocouples	29	2	2	6	2	2	6	2	2	
MSA Detector	15							1	1	
Shell Detector	2	1	1							
TSI Detector	4			2			2			
Anarad Detector	1				1					
LLL IR Detector	1					1				
CGC LINDAR	1									
JPL Laser	1									1
JPL TBDR	2									2
Grab Sampler	12	1	1	3	1	1	3	1	1	
Distance from Spill Point, m		7.6	15	30	33	50	55	91	91	55
Location		water	water	edge	edge	land	land	land	land	land

Notes: 1. There were other MSA Detectors in a second array.

2. In Tests LNG 20 and 21, Station 4 was moved from the pond edge to the land, 40 m from the spill point.

BIBLIOGRAPHY

1. Boni, A.A., M. Chapman, and J.L. Cook, "A Study of Detonation in Methane/Air Clouds," presented at the Sixth International Colloquium Gas Dynamics of Explosions and Reactive Systems, Stockholm, Sweden (22-26 August 1977)
2. Bull, D.C., J.E. Elsworth, G. Hopper, and C.P. Quinn, A Study of Spherical Detonation in Mixtures of Methane and Oxygen Diluted by Nitrogen," Journal of Physics D": Applied Physics, 9 pp 1991-2000 (1976)
3. Burgess, D.S., J. Biordi, and J. Murphy, "Hazards of Spillage of LNG Into Water," prepared by the U.S. Bureau of Mines for the U.S. Coast Guard, NTIS AD-754498 (September 1972)
4. Burgess, D.S., J.N. Murphy, and M.G. Zabetakis, "Hazards of LNG Spillage in Marine Transport," prepared by the U.S. Bureau of Mines for the U.S. Coast Guard, NTIS AD-705078 (February 1970)
5. Department of Energy, "An Approch to Liquefied Natural Gas (LNG) Safety and Environmental Control Research," DOE/EV-0002 (February 1978)
6. Department of Energy, "Liquefied Gaseous Fuels Safety and Environmental Control Assessment Program: A Status Report," DOE/EV-0037 (May 1979)
7. Lind, C.D., "Explosion Hazards Associated with Spills of Large Quantities of Hazardous Materials, Phase I, "Prepared by the Naval Weapons Center, China Lake, California, for the U.S. Coast Guard, NTIS AD-A001242 (October 1974)

8. Lind, C.D., and J.C. Whitson, "Explosion Hazards Associated with Spills of Large Quantities of Hazardous Materials, Phase II, "Prepared by the Naval Weapons Center, China Lake, California, for the U.S. Coast Guard, NTIS AD-A047585 (November 1977)

9. Lind, C.D., and J.C. Whitson, "China Lake Spill Tests," prepared by the Naval Weapons Center, China Lake, California, for the U.S. Coast Guard and the Deparment of Energy (1979)

10. Schneider, A.L., "Liquefied Natural Gas Safety Research Overview," presented at the 1978 American Gas Association - Cryogenic Society of America, LNG Terminal & Safety Symposium, San Diego, California (12-13 October 1979)